

October 17, 2003

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Re: Twenty-Second Monthly Report #NDJ-2-30630-11

Dear Harin,

This letter comprises the monthly technical status report for ITN's subcontract # NDJ-2-30630-11, "Plasma-Assisted Coevaporation of S and Se for Wide Band Gap Chalcopyrite Photovoltaics", under the Thin Film Partnership Program. The reported work was performed during the tenth month of phase 2 for this contract (twenty-second month overall), which is September 7, 2003 through October 7, 2003. This report describes activities performed by ITN, as well as those performed by lower-tier subcontractor Colorado School of Mines (CSM), under the direction of Dr. Colin Wolden.

## **1. Program Goals and Approach**

Our primary objective under this program is to determine if the chalcogen in CIGS co-evaporation can be delivered more effectively by activation with a plasma. Possible advantages of plasma-assisted co-evaporation (PACE) are

- increased utilization of chalcogens,
- decreased deposition temperatures,
- decreased deposition times, and
- increased ability to tailor S/Se ratio.

University researchers at CSM are developing and testing the fundamental chemistry and engineering principles. Industrial researchers at ITN are adapting PACE technology to CIGSS co-evaporation and validating PACE process for fabrication of thin film PV.  $\text{In}_2\text{Se}_3$  films, which are used as precursor layers in high-efficiency CIGS depositions, are the first test case for the examining the advantages of PACE listed above. Gradually, this examination is being extended to the complete high-efficiency three-stage co-evaporation process.

## **2. ICP Source Development**

As reported in previous months, plasma-activated chalcogen delivery in the co-evaporative environment is being investigated using two approaches. In the first approach, chalcogen flux delivered to the plasma is controlled mainly by the effusion source

temperature. Advantages of this first approach include large source capacity and capabilities for high Se pressures. In the second approach, chalcogen flux is controlled mainly by the temperature of a hot carrier gas that flows over Se-coated plates. Advantages of the second approach include reduced thermal time constants and reduction of condensation between the Se source and the ICP device. This month, progress was made in the implementation and testing of both source designs.

For the first time, the design based on a thermal effusion source (first approach) was operated with acceptable control in conjunction with the quartz plasma tube and Ar gas. This control was achieved by 1) avoiding Se condensation via heating the Ar gas prior to its entry to the source, 2) tuning the proportional integral derivative (PID) control loops, and 3) utilizing the improved Se pot described last month. Figure 1 shows Se rate as a function of time for the source, both with and without the quartz plasma tube in place. Rate was measured by a quartz crystal microbalance (QCM) placed 1" above the source opening. Se rate with the quartz tube in place is somewhat irregular compared to the rate without, but is still inside an acceptable envelope for CIGS co-evaporation. Source temperatures at the Se melt and at the source nozzle are also shown in Figure 1.

At CSM, an improvement to the control of the ICP selenium source using hot carrier gas (second approach) is being made. A high temperature (375 °C) gas metering valve was integrated into the selenium delivery source to provide more precise control over selenium flux. The source is assembled and its calibration using optical emission spectroscopy and copper selenization is underway.

### **3. Co-Delivery of Plasma-Activated Species**

Several advances were made toward co-delivery of plasma-activated species.

At CSM, the In flux in the PACE chamber was carefully calibrated, to gain a precise knowledge of the ratio of chalcogen to metals during co-deposition. Figure 2 graphs in-situ QCM measurements versus ex-situ thickness measurements performed by profilometry. Two sets of data are shown. One is obtained at ambient conditions and the other at a substrate temperature of 200°C. In general, the profilometry values scale with the QCM. However, for the same QCM flux, the films deposited on the heated substrate were always thicker than films on a cold substrate. It is hypothesized that the 200°C films are less dense. (The QCM measures mass, and a constant density was assumed in determining rates.) Optical microscopy shows that the films deposited at higher substrate temperature are much rougher, consistent with the hypothesis. Currently a microbalance is being used to obtain film masses and hence compare densities. Figure 3 shows that the indium flux may be controlled over a range from 0.2 – 20 Å/s. The data in Figure 3 are obtained from five charges of the same boat. As expected, the deposition rate decreased slightly as the boat was used.

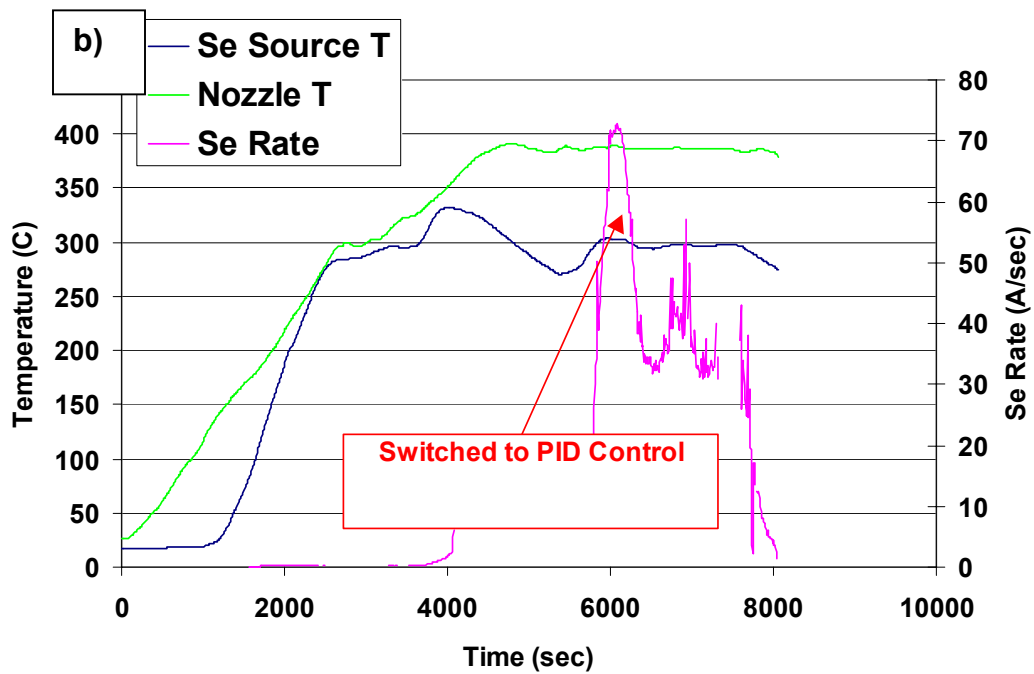
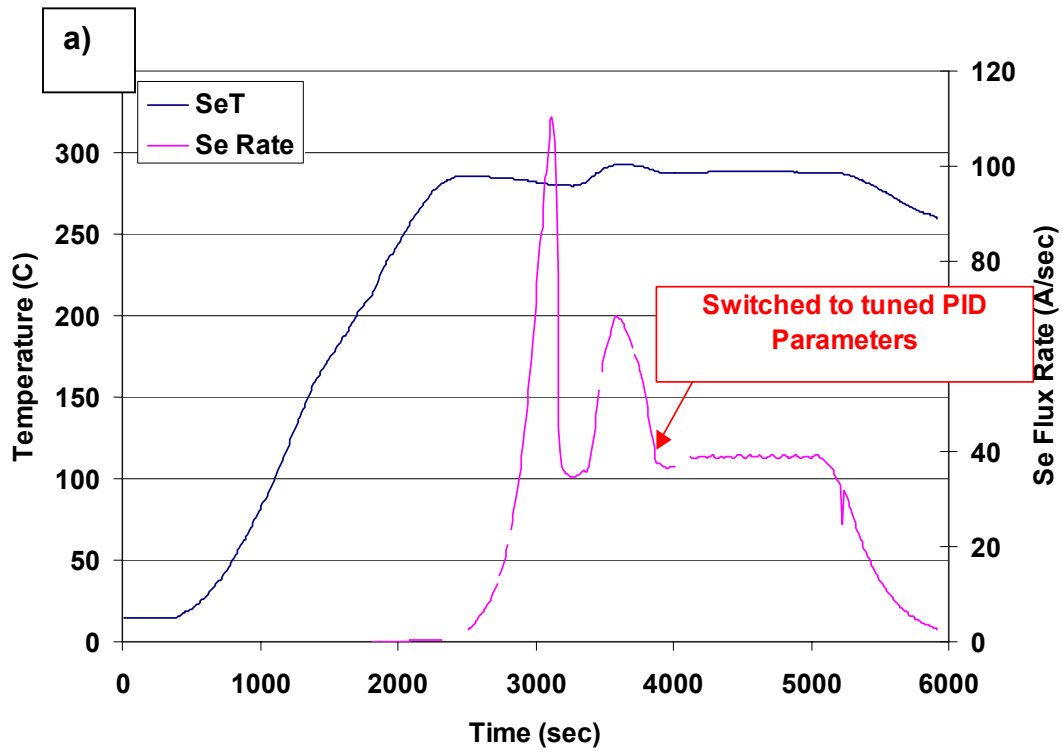


Figure 1: Se rate from PACE effusion source a) without and b) with quartz reactor tube. Effusion source temperature is also shown.

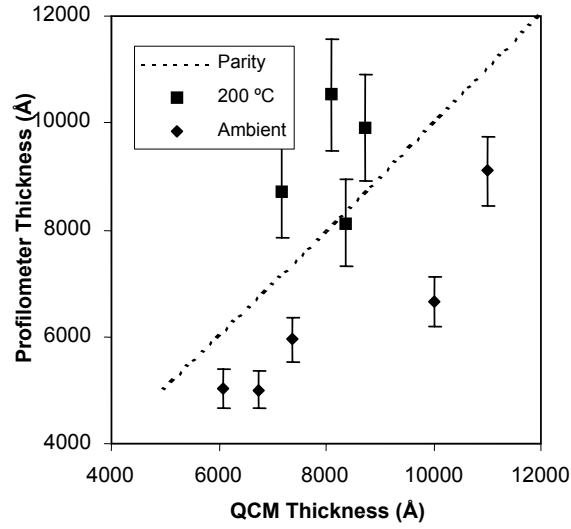


Figure 2: QCM vs. profilometer calibration of film thickness under deposition conditions.

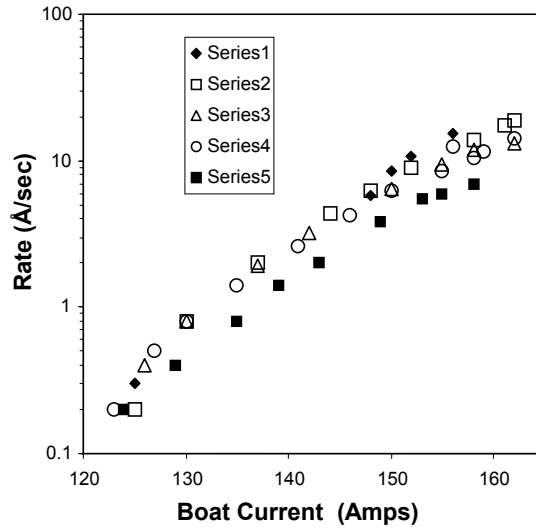


Figure 3: Deposition rate as a function of current for sequential use of the same boat.

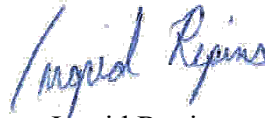
Source lifetime and operation issues are also being addressed in the PACE chamber. Stainless steel shielding was fabricated and installed to separate the indium evaporation source and the selenium ICP source. It prevents indium deposition from occurring on the ICP source. It is also well grounded, acting as a Faraday cage to limit RF noise from the plasma. This grounding allows operation of the ICP source without influencing the QCM, substrate heater, evaporation source, or instrumentation.

At ITN, ways to shorten the effusion-based PACE source to fit in a typical CIGS co-evaporation chamber are under consideration. The current source stack - including the Se pot, tee for Ar introduction, and quartz reactor tube – is nearly 16” long. Several possibilities exist for reconfiguring the source to an acceptable size. Determination of “acceptable size” depends not only on chamber dimensions, but also on Se flux and uniformity as a function of distance from the reactor tube aperture. These issues are currently being explored.

#### **4. Team Activities**

ITN and CSM participate in CIS team activities. This month’s activities relate to planning for the November meeting, and follow-up discussion and sample exchanges from the previous month’s capacitance characterization of team samples.

Best Wishes,



Ingrid Repins  
Principal investigator  
ITN Energy Systems

Cc: Ms. Carolyn Lopez; NREL contracts and business services  
Dr. Colin Wolden; CSM technical lead